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## Technical Report

### TR-2114-ENV

## DEVELOPMENT OF A SENSOR TO DETECT AFFF IN SHIP BILGE WATER

by

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May 2000

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## EXECUTIVE SUMMARY

A sensor system was developed to detect the presence of foam producing chemicals. The sensor was developed primarily to detect the presence of aqueous film forming foam (AFFF) in bilge water off-loaded from a ship to a shore-side wastewater treatment plant. The foam sensor uses a combination of photo-optical and acoustic range measuring devices to determine the density and height of a column of foam produced by aeration of the wastewater sample. These data are used to estimate the concentration of AFFF in the wastewater sample. The sensor system can detect concentrations of AFFF as low as 10 ppm in approximately 45 seconds. Solutions containing higher concentrations of AFFF are detected in less time. When the concentration of AFFF exceeds a preset value, a switch within the sensor system is closed. This switch closure can be used to control functions such as operating a valve to divert the contaminated wastewater stream to a storage tank or a specialized treatment process, or to control other treatment plant processes.

The AFFF sensor is shown in Figure 1. The sensor is enclosed in a weatherproof cabinet that measures approximately 2 feet wide by 4 feet high by 8 inches deep. Parts and materials for the system cost approximately \$2,000.00

A prototype AFFF sensor was installed at the Oily Wastewater/Waste Oil Treatment Plant at the Naval Station, Mayport, Florida. The prototype unit is currently undergoing extended field testing.



Figure 1. Prototype AFFF sensing unit.

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## **OBJECTIVE**

The objective of this project was to develop a sensor capable of detecting the presence of aqueous film forming foam (AFFF) at low concentrations (less than 50 ppm). Desired attributes of the sensor are high reliability, low maintenance, low cost, and small size.

## **BACKGROUND**

Aqueous film forming foam, or AFFF, is a generic name given to a class of chemical compounds that are mixed with water to form a more effective fire fighting agent. AFFF concentrate is added to the water stream being directed at a fire. The resulting mixture forms dense white foam that reduces the amount of air reaching the fire. AFFF is frequently used aboard ships and aircraft crash/rescue vehicles because of its ability to smother liquid fuel fires. As a result of using AFFF in fire fighting training exercises aboard ship (and the unauthorized use of AFFF as a cleaner), the compound sometimes finds its way to the ship's bilge.

When a ship comes into port, it may discharge its bilge water to a shore-side wastewater treatment plant. If the ship's bilge water contains AFFF, the operating conditions of the plant may be upset, resulting in discharges from the plant that exceed the limits of the plant operating permit. There have been incidents of the Navy receiving notices of permit violation from State environmental agencies for out-of-limit waste treatment plant discharges caused by AFFF.

AFFF is not considered to be toxic to humans, but it can harm small organisms such as the eggs and larvae of aquatic animals. Also, AFFF has been demonstrated to kill beneficial bacteria in wastewater treatment plants. In addition, foam formed by AFFF can cause false readings from flow and level sensors that control waste treatment plant processes. For these reasons, it is very desirable to prevent AFFF from entering a wastewater treatment plant.

If a reliable AFFF sensor system can be developed, it can be used to determine if AFFF is present in the wastewater ships send to a shore-side treatment plant. If AFFF is detected in the waste stream, the wastewater can be diverted to a specialized treatment process or to holding tanks for disposal as a special waste stream.

## **APPROACH**

Several companies manufacture AFFF. The formulations are generally trade secrets but are known to contain urea, alkyl sulfates, amphoteric fluoroalkylamide, perfluoroalkyl sulfonate salts, triethanolamine, and other compounds. AFFF is sold as a "concentrate." The amount of active ingredients in AFFF concentrate is usually 3 percent; the balance is water. Thus, commercially available AFFF concentrate contains about 30,000 parts per million (ppm) of active ingredients.

The authors measured the concentration of surfactants in samples of AFFF using a standard wet chemistry test called the methylene blue active substances test (EPA Method 425.1). The MBAS test comprises three successive extractions from acid aqueous media containing excess methylene blue into chloroform, followed by an aqueous backwash and measurement of the

intensity of the blue color in the chloroform by spectrophotometry at 652 nm. The MBAS test is useful for estimating the anionic surfactant content of wastewater. Alkyl sulfonates and sulfates are common anionic surfactants and are present in AFFF. However, cationic surfactants, amines, and sulfides (often present in wastewater) also react with the methylene blue, making accurate analysis difficult. The MBAS tests were performed by a commercial analytical laboratory on samples of AFFF solutions prepared by the authors. Samples of 3 percent AFFF concentrate were mixed with distilled water to produce a 50 ppm solution of active ingredients. Samples of this mixture produced surfactant concentrations of 72 to 78 ppm using the MBAS test. Similar tests performed on three samples of a 1.5 ppm solution of AFFF active ingredients produced results ranging from 1.9 ppm to 2.3 ppm.

A literature search was performed to identify previous and current efforts in AFFF sensor development. Many of the past efforts focussed on finding a unique chemical or physical characteristic of AFFF that could be used as a sensed variable. The authors performed experiments on some of the properties of AFFF including testing solutions of AFFF for fluorescence, change in index of refraction, electrical conductivity, etc. These experiments confirmed that AFFF has no easily measured unique characteristic. It may be feasible to identify AFFF by high-pressure liquid chromatography or other specialized chemical analysis methods. However, these methods were judged to be too expensive, complex, and time consuming for real time field use.

The only readily measured characteristic of AFFF appears to be its ability to generate a large volume of foam at small concentrations. It was determined that measuring the foam forming capabilities of a wastewater sample is the most promising approach to developing a real time AFFF detection system.

## RESULTS

The development of the AFFF sensor described in this report was based on a series of empirical developments.

The basis for the initial experiments was a surfactant measuring device designed at Los Alamos National Laboratory (LANL) (References 1 and 2). The LANL device is illustrated in Figure 2. The sensor is a piece of custom glassware made from a laboratory apparatus called an air washer. The LANL device works as follows: liquid containing the surfactant is introduced at the top of the vessel through a "tee" shaped pipe that distributes the sample so that it runs down the walls of the vessel. This flow arrangement is intended to keep the walls of the vessel clean. The sample collects at the bottom of the vessel and is aerated by air forced through a porous plug. An overflow port in the side of the vessel keeps the liquid level constant. The aerated sample produces a column of foam in the vessel. The column grows until it reaches an equilibrium height. The equilibrium height (for a specific surfactant) is a function of the concentration of the surfactant in the water sample, the amount of time the sample is in the vessel, and the amount of aeration air. Under conditions of constant sample flow rate and aeration, the equilibrium height can be correlated with the concentration of surfactants. LANL proposed measuring the equilibrium height of the foam column with a series of photo-optical sensor pairs. A photo-

optical sensor pair consists of a light emitting diode and phototransistor separated by a gap. When the beam of light from the light emitting diode to the phototransistor is interrupted, the transistor acts as a closed switch, thereby completing the level sensing circuit.

The first experiments were based on the LANL design. Several variations on the LANL design were fabricated from standard clear polyvinylchloride (PVC) pipe and pipe fittings (Fig. 3). Plastic was used because of the difficulty and expense of obtaining custom glassware.

Numerous bench top experiments were performed with these designs, varying pipe diameter, inlet flow distribution, outlet design, and aeration. Typical results are presented in Figures 4, 5, and 6. Figure 4 shows the equilibrium foam height achieved by aerating AFFF solutions of various concentrations. This figure illustrates that stable foam height is a function of AFFF concentration; the greater the concentration, the higher the equilibrium foam height. Figure 4 also shows that it may take 15 to 20 minutes for the foam height to reach an equilibrium level. Because of the long period required to reach the equilibrium foam height, a sensing system based on equilibrium foam height was judged impractical for real-time control applications.

A sensor based on the transient response of the foam column was determined to be a more practical approach. Figure 5 shows transient response of a column of AFFF foam. The response of the foam column between 0 and 120 seconds is the region of interest for these studies.

It was observed that two distinct types of foam are produced by AFFF. Below concentrations of about 20 ppm, AFFF produces what is known as "dry" foam. In dry foam, the volume occupied by the foam material is small. There is little liquid in the walls of the bubbles, so the walls may be regarded as having negligible thickness. These thin walls arrange themselves into cells in a manner that minimizes the surface energy. The cells in a dry foam are relatively large polyhedrons, under ideal conditions a 14-sided shape called a truncated octahedron (see Reference 3). At higher AFFF concentrations, the liquid content is substantially higher. This additional liquid acts as a contact barrier between the foam bubbles. When foam has a high liquid content, the individual bubbles have much more freedom to form the minimum energy shape than in dry foam, because the bubbles do not directly touch one another. If there is enough liquid, each bubble will independently minimize its surface energy. Under these conditions, the shape of the minimum energy configuration is a sphere. Thus, at higher AFFF concentrations, the foam appears to be a mass of spherical bubbles in a liquid matrix. This type of foam is much stronger structurally than dry foam. Wet foams are also more opaque than dry foams. These differences in foam properties complicate the process of designing a device that responds equally to both high and low concentrations of AFFF.

It was also observed that AFFF forms very persistent residual foam. If AFFF foam is kept in a humid atmosphere (such as the closed container), most of the water will drain out of the foam – often leaving residual foam in the tube. This residual foam can persist for several days and is strong enough to support lightweight objects.

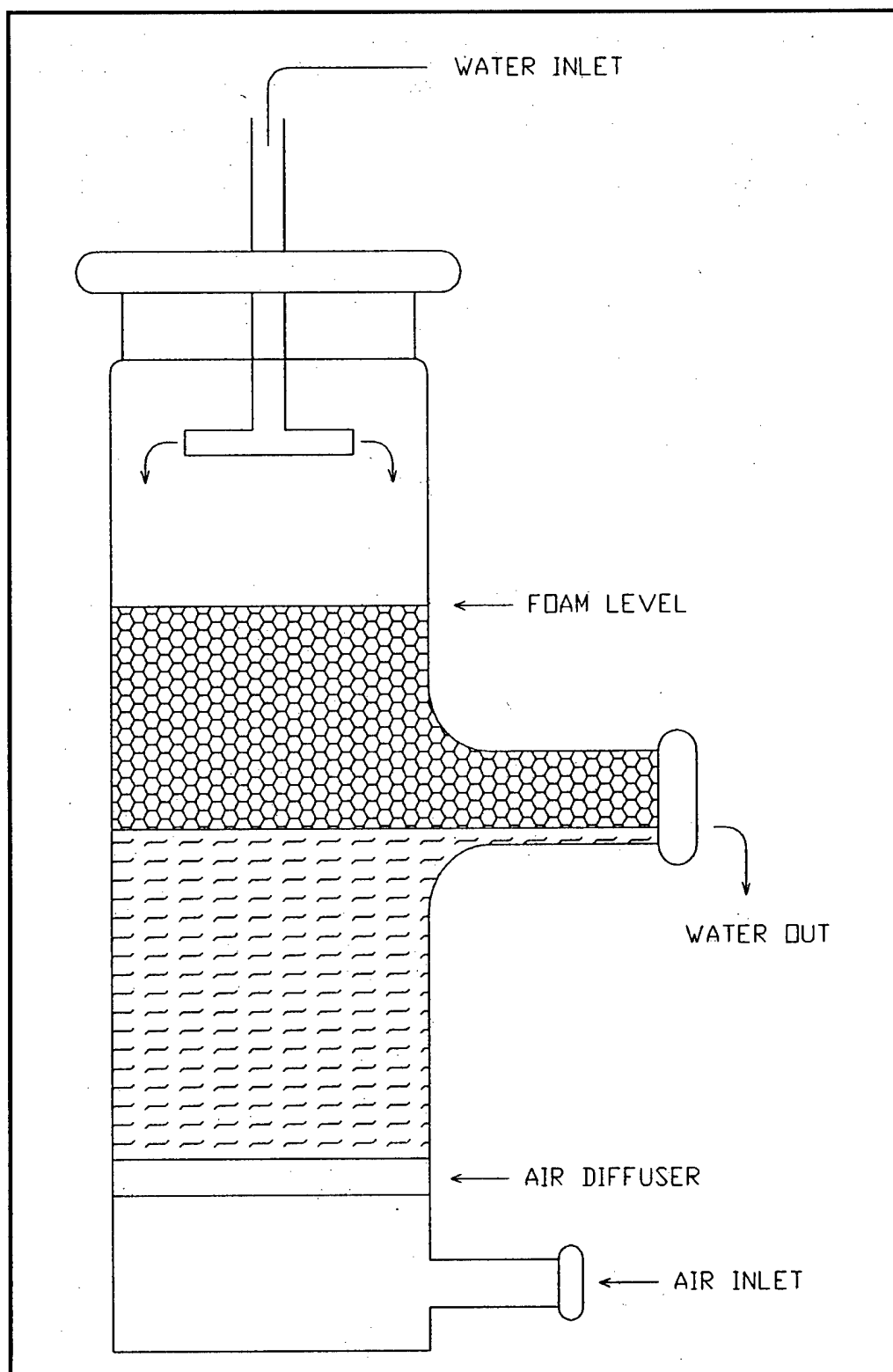


Figure 2. Sketch of LANL foam measuring device.



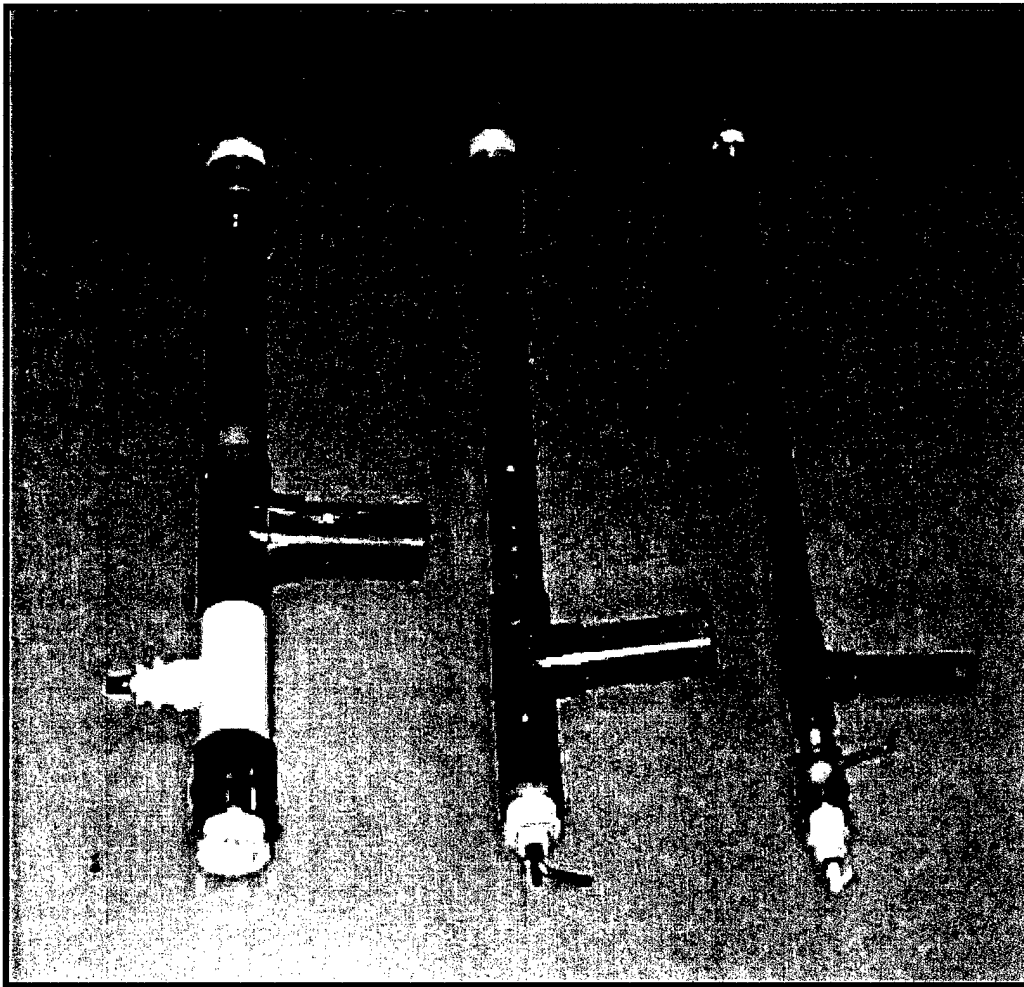


Figure 3. Examples of early prototype AFFF sensors.

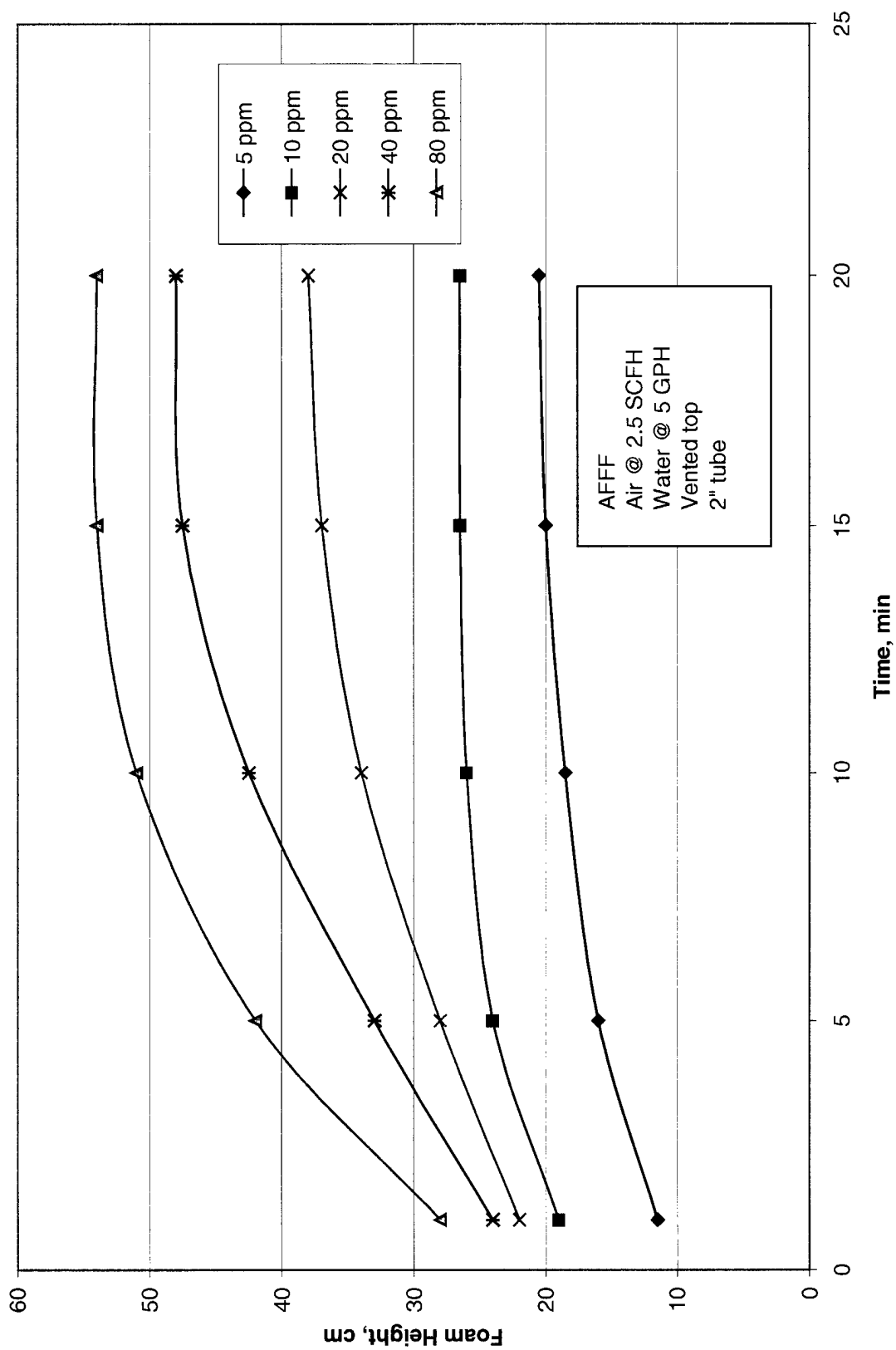


Figure 4. Equilibrium foam height as a function of AFFF concentration.

# Transient Response of AFFF

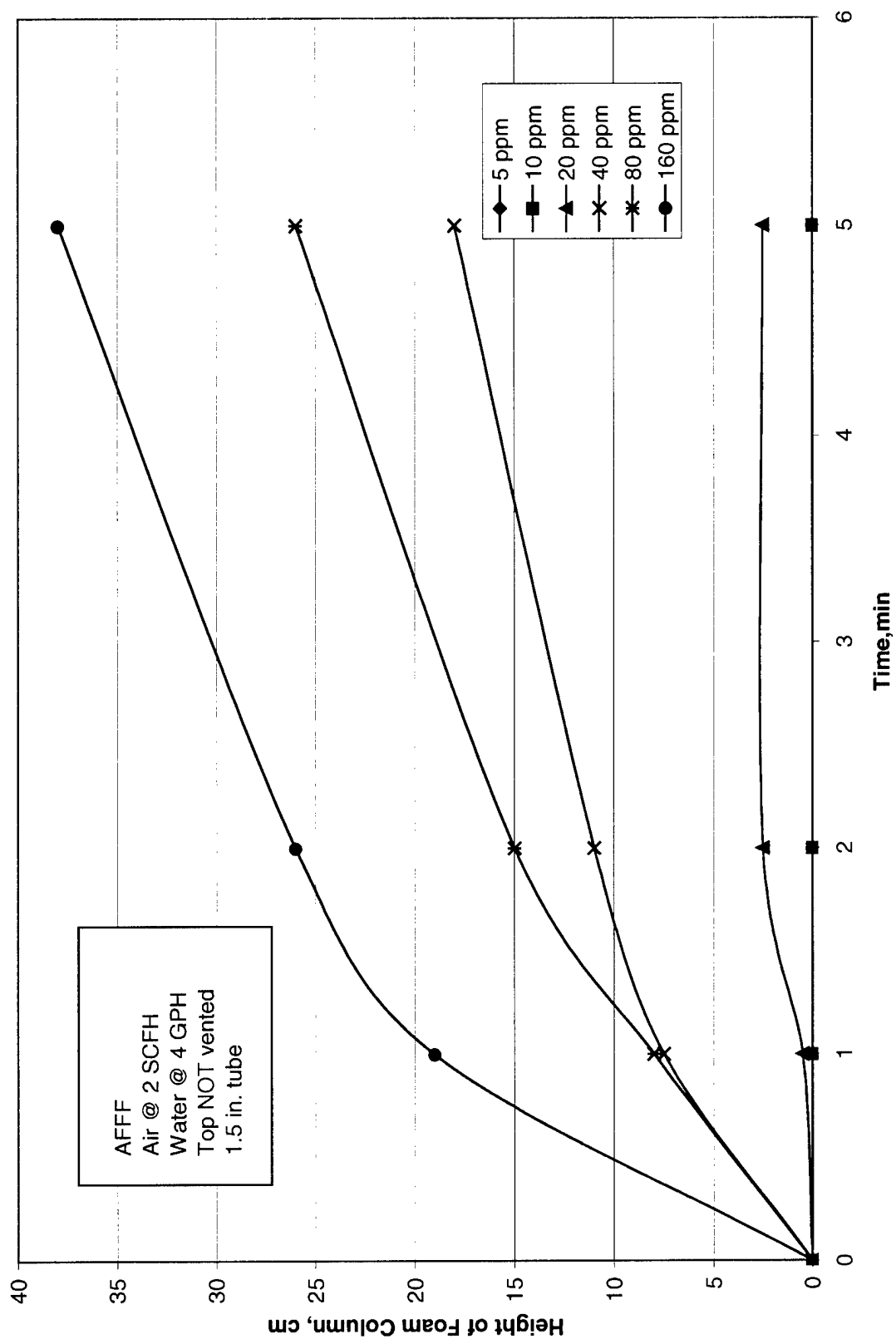


Figure 5. Transient response of a column of AFFF.

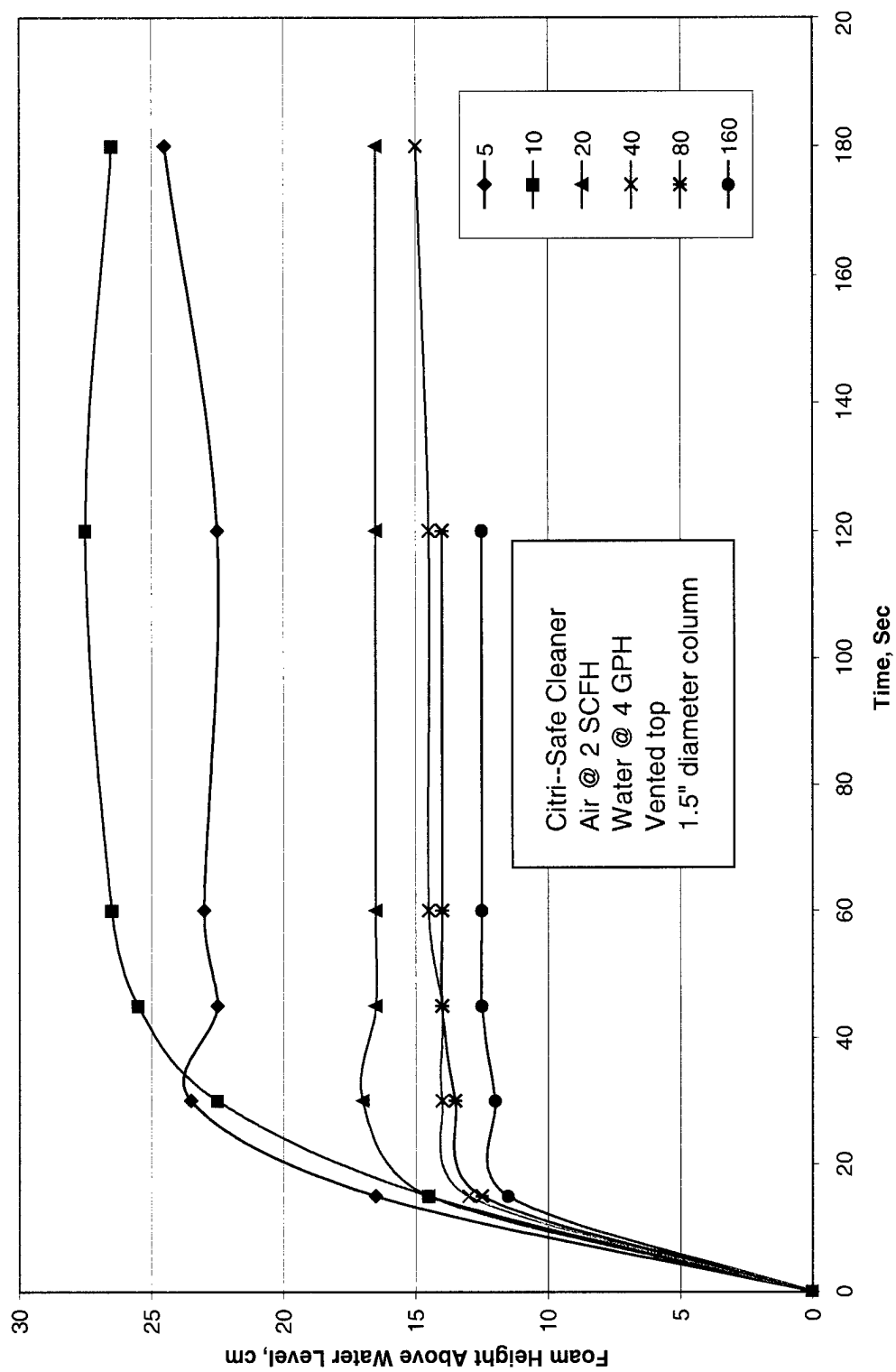


Figure 6. Transient response of a column of citrus cleaner foam.

AFFF is not the only compound likely to be found in bilge water that generates large amounts of foam. Figure 6 presents similar results for a common citrus-based cleaner-degreaser. Note, for this compound, greater concentrations, result in *lower* equilibrium foam heights.

Most common soaps and detergents do not foam as much as AFFF. Experiments with a common dish washing detergent (Ivory Liquid®) indicate that it takes about 400 times the concentration of dishwashing liquid to make the same amount of foam as AFFF.

Based on the experiments noted above, a foam sensor system was designed, built, and evaluated. This sensor (Figure 7) used two photo-optical pairs to detect the height of a foam column at two points: a low set point and a high set point. The outputs from these photo-optical switches were connected to a commercial tank level controller. When the height of the foam column reached the high set point, the controller would close a relay (that could, for example, be used to operate a flow diversion valve). The relay remained closed until the level of the foam dropped below the lower set point.

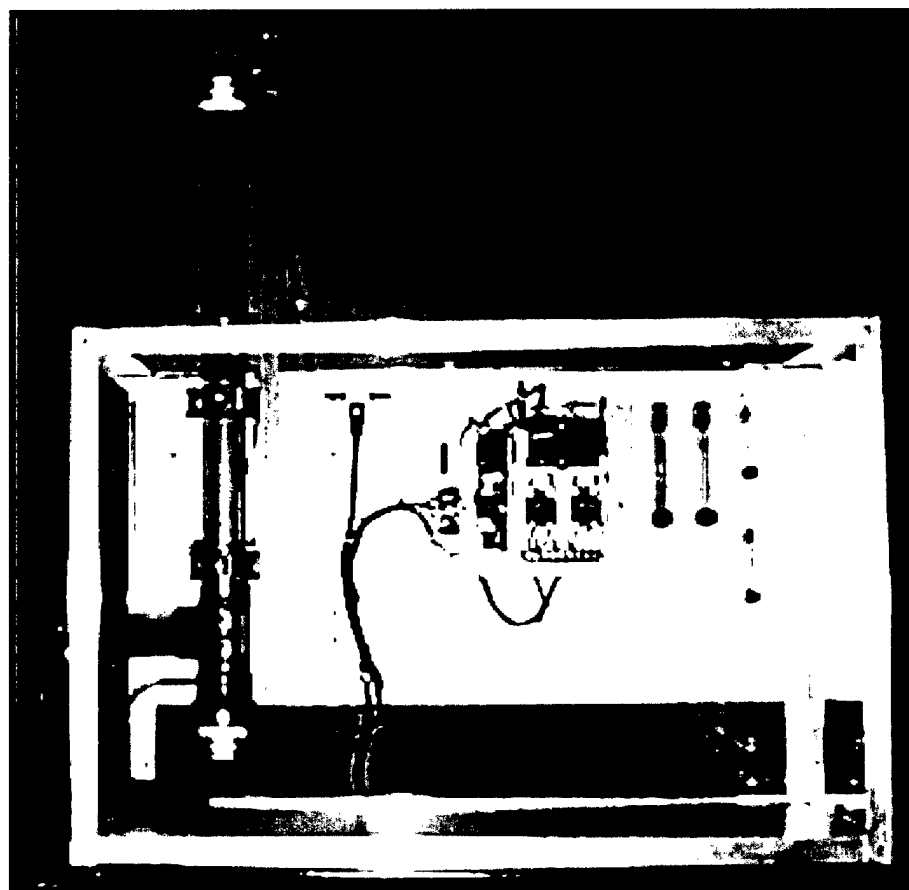


Figure 7. Prototype AFFF sensor system using tank level controller.

Numerous problems with this design were identified during experiments. First, at low concentrations of AFFF, the foam was transparent to the light beam, i.e., the unit could not reliably detect the presence of low concentrations of AFFF. Also, gaps would develop in the column of foam that would result in false signals to the controller. For example a gap, or break, in the foam column would develop under certain conditions and result in the upper set point switch being closed, while the lower set point switch would be open. This is a logical inconsistency that a simple tank level controller cannot resolve.

Also, it was realized that it may be difficult to keep the optical path clear. Oil, dirt, algae, and other contaminants may collect on the walls of the transparent vertical tube, causing the light beam to be interrupted when no foam is present. For this reason, it was decided to measure the height of the foam column by a method that did not require that the walls of the sample tube be transparent.

These experiments also showed that, while it was fairly easy to detect the beginning of an AFFF event, it was not easy to detect the end of an AFFF event. (An AFFF event is the presence of AFFF in the wastewater line.) The problem is caused by the high sensitivity of the sensing method and the way the sample is collected. For example, suppose the wastewater line carries bilge water containing 200 ppm of AFFF. The results presented in Figure 5 indicate that AFFF in this concentration could be easily detected by measuring foam height. However, the results also show that it is also possible to detect AFFF at 10 ppm concentration. Thus, if the wastewater line switched from a source that contains AFFF and to a source that does not contain AFFF, there would be a long delay while the sample in the sensor is slowly diluted by the incoming water to a level that the sensor could no longer detect. This could mean that a large amount of wastewater that does not contain AFFF would be unintentionally identified as being contaminated. This could greatly increase the cost of treatment and disposal.

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These considerations led to the third generation design (Figure 8). The third generation design incorporates an acoustic range finder to measure the distance between the top of the foam column and the end of the sensor. The use of an acoustic range sensor eliminates the problem caused by low foam density, air gaps in the foam column, and occlusion of the sample tube. The acoustic sensor provides a true measure of position of the top of the foam column, whereas photo-optical sensors provide information only about whether the beam of light is blocked.

In addition to the use of acoustic measurement of foam column height, this design incorporates a more complex sampling method. To address the problem of rapid detection of the end of a foam event, a discrete sampling method was developed. In this method, a time series of separate wastewater samples is collected, analyzed, and discarded. In this way, a completely new sample of wastewater is periodically input into the sensor. This is in contrast to the continuous sampling method where the input stream slowly changes the sample in the sensor.

This design underwent extensive testing using a test stand designed specifically to simulate the changeover from AFFF contaminated water to clean water. The test stand is shown in Figure 9. The sensor system can draw a test sample from either of the two large tanks. A circuit of interval and time delay relays determines which tank the sample is drawn from and for how long.

The sensor control logic was initially implemented using electro-mechanical relays, delay timers, and interval timers (the large gray panel located below the AFFF sensor in Figure 9). Later designs replaced the relay logic with a programmable logic controller (PLC). The PLC is programmed by means of a link to a personal computer and uses standard ladder logic and symbols. This allows the program to be changed easily and quickly.

The final AFFF sensor design incorporated the lessons learned from these tests. Diagrams of the final AFFF sensor design and of a typical installation are presented in Figures 10 and 11.

When the bilge water transfer pump comes on, a switch closure activates the AFFF sensor system and begins the testing process. As long as the transfer pump is operating, a small slipstream of wastewater (about 0.33 gallons per minute) flows from the waste water line to the sensor. The wastewater sample enters the bottom of the sensing chamber through a normally open 3-way solenoid valve.

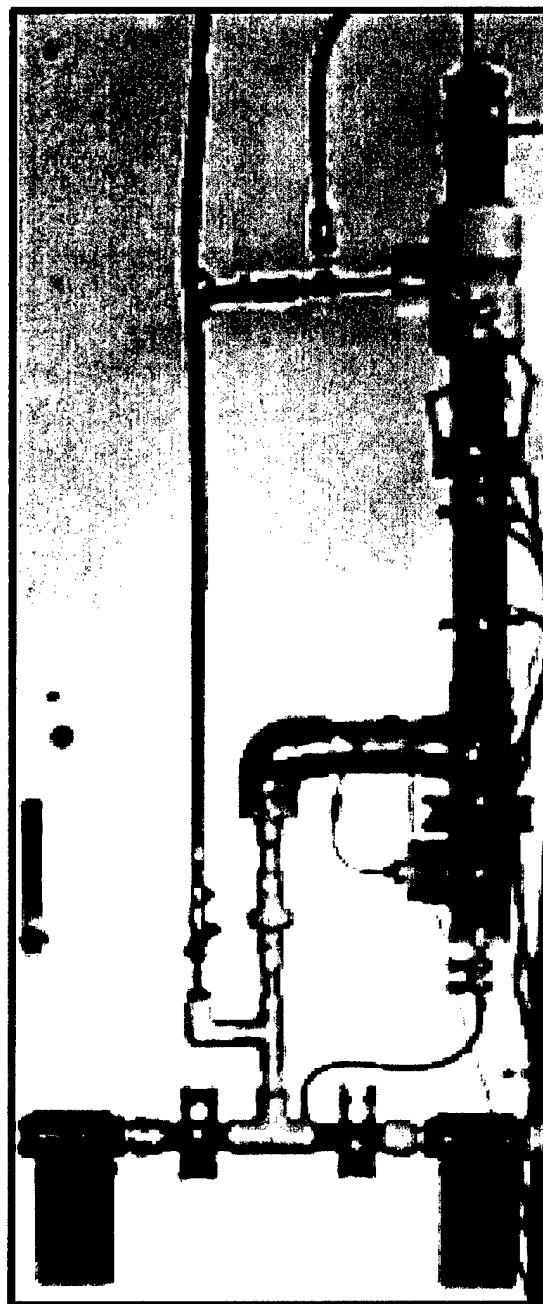


Figure 8. Third generation AFFF sensor.

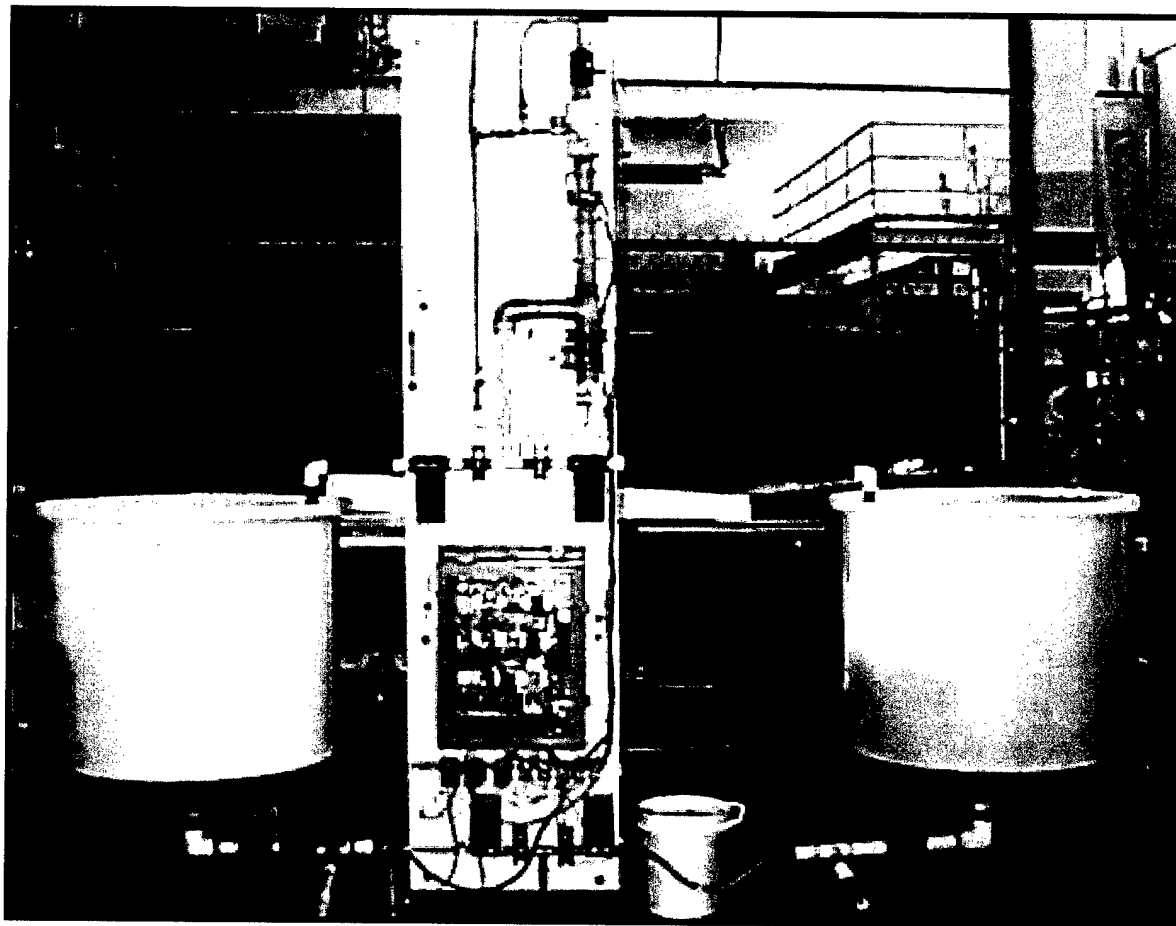


Figure 9. Prototype AFFF sensor on test stand.

The sample fills the sensing chamber until it reaches the overflow port in the side of the chamber. The overflow port is connected to a damping chamber. The damping chamber is a horizontal tube with a weir at each end. The damping chamber moderates the flow out of the sample chamber and stabilizes the height of the foam column. (It was discovered during the early experiments that, without the presence of some damping at the discharge port, the height of the foam column would build up to a critical height and then suddenly collapse and discharge through the port. The outlet port damping chamber eliminates this problem.) Discharge from the damping chamber goes to a drain or back to the wastewater line.

The sample in the sensing chamber is aerated by means of an airstone. Air for the process is supplied by a small aquarium air pump. Aeration of the sample forms bubbles in the water. The surfactants in AFFF adsorb at the water-gas interface and form foam. The column of foam rises, lifting a lightweight, molded polystyrene float. The float serves as a firm target for the acoustic range sensor.



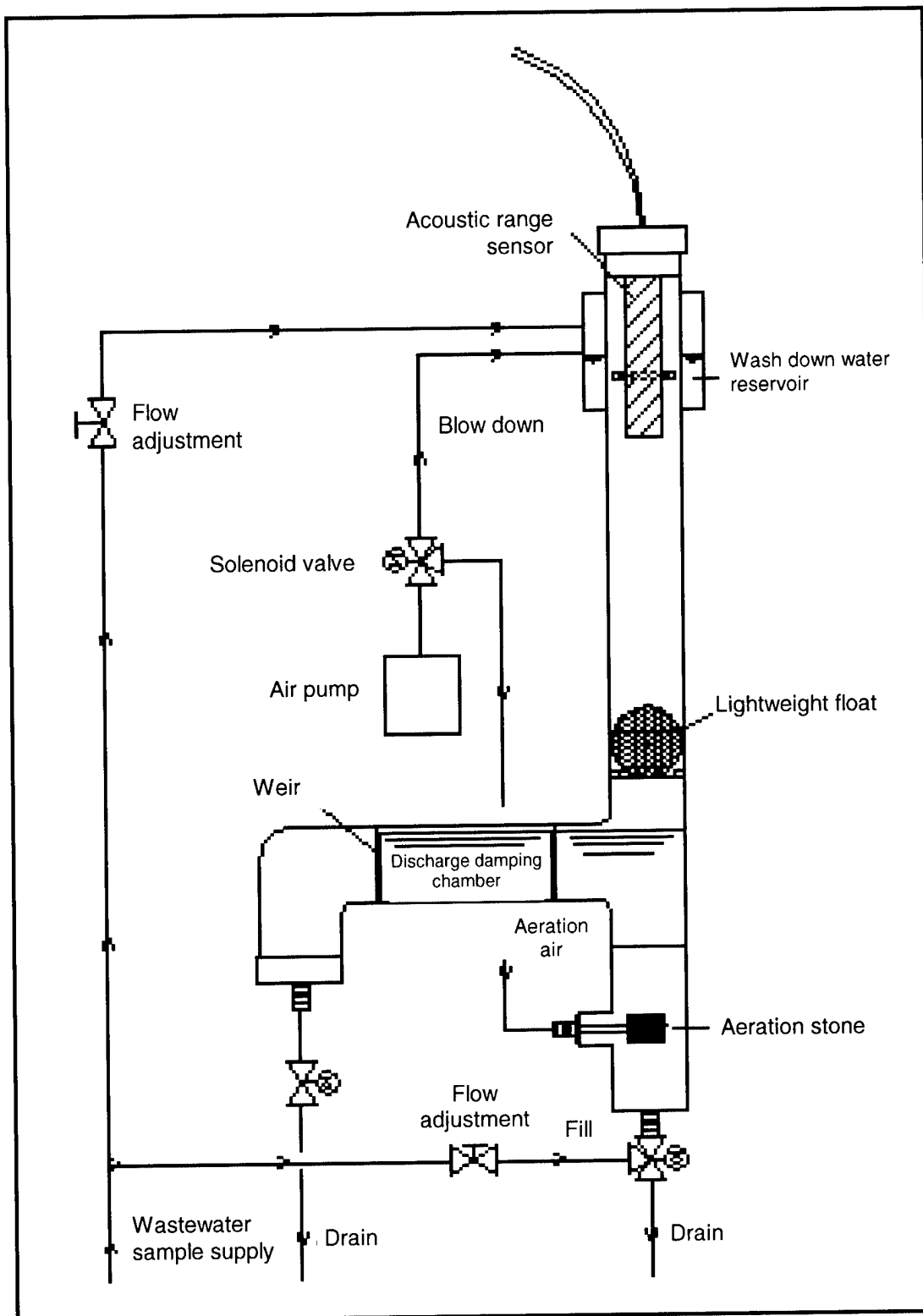


Figure 10. Sketch of AFFF sensor.

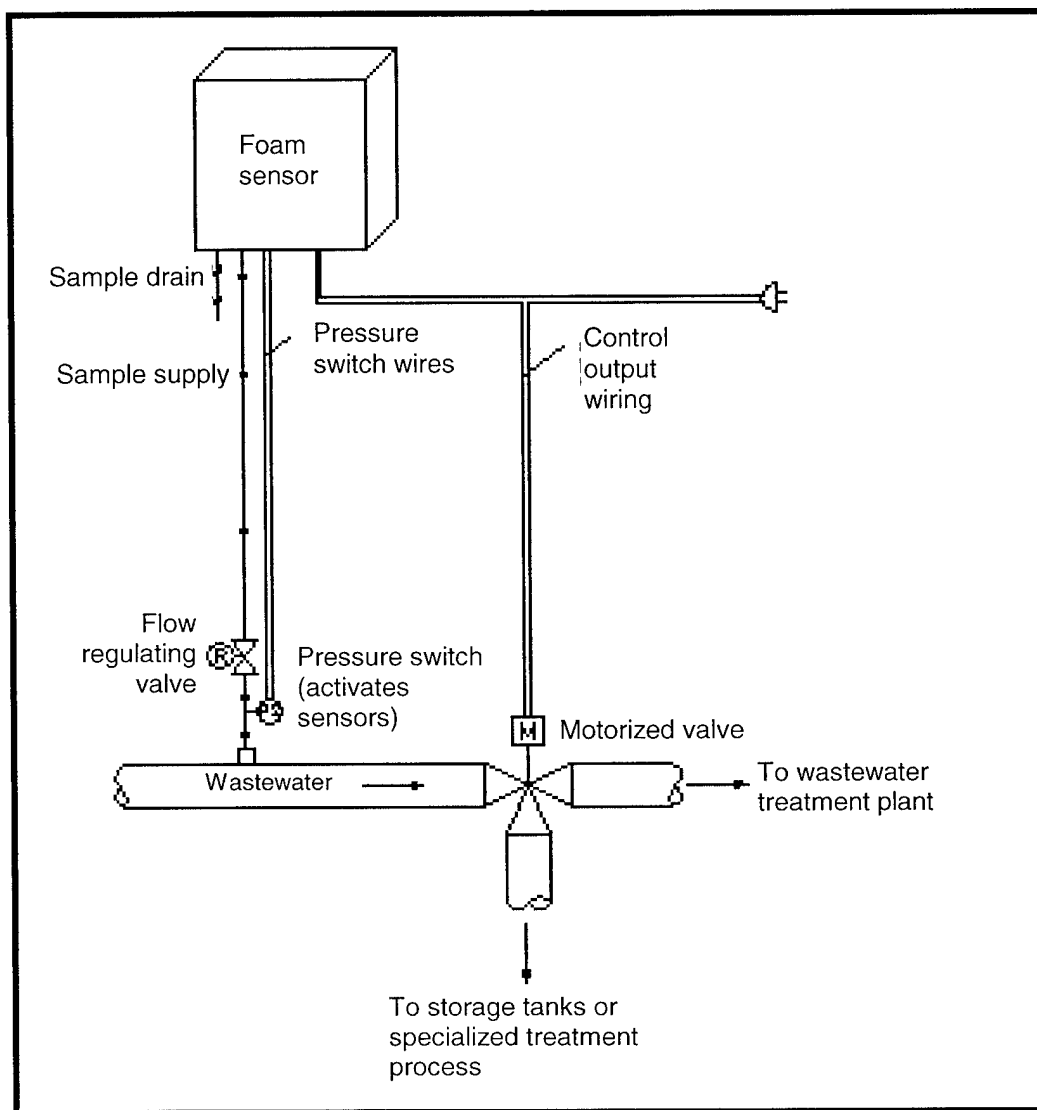


Figure 11. Sketch of AFFF installation.

An acoustic range sensor, located at the top of the column, produces pulses of sound at a frequency of 17 kHz. The time it takes for a sound pulse to travel from the end of the sensor to the float and return is measured. From the travel time, the distance from the end of the acoustic sensor to the float can be accurately determined. This distance measurement is compared to three distinct set points: a low set point, a high set point, and an alarm set point. The set point distances and other characteristics of the acoustic sensor are programmed through a serial port on the device using software supplied by the manufacturer.

When the float reaches the high set point, a relay is latched. This switch closure is the output from the AFFF sensor unit and would be used to operate a valve to divert the AFFF laden wastewater away from the wastewater treatment plant. The output relay is unlatched only if the float falls below the low set point and fails to rise to the low set point within a specified period of

time. This will occur when the sensor system tests wastewater free of AFFF. If the float rises to the alarm set point, pressurized air is briefly diverted to the top of the sample column. This action forces the column of foam down to the low set point. When the low set point is reached, air is again directed to the air stone.

Periodically (approximately every 2 minutes), the fill and air valves close. Pressurized air is directed to the top of the sample column. This action forces the column of foam and the wastewater sample out of the sensor. After the sample is purged, the fill and air valves open and the sampling process begun anew. This is the sequential sampling process mentioned earlier.

A small portion of the wastewater sample is directed to a chamber located at the top of the sample column. Within the chamber, the wall of the sample tube is perforated with a series of small holes around the circumference. These holes permit the wastewater sample to run down the interior wall of the sample tube. This “wash down” water helps to keep foam from adhering to the wall of the tube and washes away any particles that may become attached to the interior of the column.

The amount of foam generated under a specific set of conditions depends on (1) the concentration of AFFF in the sample, (2) how long the sample is aerated, and (3) the rate of aeration air flow. In general, the higher the AFFF concentration, the longer the sample remains in the aeration chamber (i.e., the lower the sample flow rate) and the more air that is forced through the sample, the more foam will be generated. The set point of the AFFF sensor system can be most easily set by adjusting the rate of flow of aeration air. The procedure for setting the sensor to detect concentrations of AFFF above a threshold value is as follows. A solution of AFFF of the threshold concentration is prepared. The aeration air supply is shut off. The AFFF solution is then pumped through the sensor system until all parts of the unit contain solution of same concentration. The aeration air bleed valve is then opened until sufficient foam is produced (in the desired response time) to raise the float to the high set point. The desired response time is the maximum time allowed to detect the presence of foam. For example, it may be the system user’s criterion to detect 50 ppm of AFFF within 30 seconds.

To a lesser extent, the set point of the AFFF sensor system can be adjusted by using floats of different weights. Foams formed by low concentrations of AFFF do not have the structural strength to lift a heavy float. It is possible to configure the system so that the float will not lift off its seat at low AFFF concentrations.

The aeration air and wash down do not immediately stop at the end of a sampling operation, i.e., when the bilge water transfer pump stops. Instead, the control system diverts the pressurized air to the top of the sample column for several seconds after the end of sampling. This “blow down” air, coupled with residual wash down water, serves to remove any remaining foam from the sample column. This prevents the target float from being suspended on top a column of residual foam. If the float were to become suspended above the low set point, the system would not shut off.

The acoustic range sensor outputs a 0 to 20 mA signal that varies linearly with the measured distance. This signal is converted to 0-5 VDC and input into a 12-bit analog-to-digital converter

circuit. The data on foam column height are combined with time data to calculate the approximate concentration of AFFF. The AFFF concentration is estimated by comparing the measured rise time of the target float with experimental results on rise time of the foam column as a function of AFFF concentration. The distance and time data are processed by a PIC 16C57 microprocessor. A real-time clock chip provides the time. The clock chip has a large capacitor wired to the supply voltage to maintain the time-date data in the event of a power failure. Results are displayed on a 16 character by 2-line back-lit liquid crystal display. The computer circuit also displays the time and date of the current AFFF event and the total number of the events since the system was activated. A typical calibration curve is presented in Figure 12. Note that the concentration of AFFF can be estimated only in the range of about 10 to 50 ppm. At concentrations less than 10 ppm, the sensor is not triggered by the AFFF. At concentrations greater than about 50 ppm, the column of foam has an approximately constant response time, independent of concentration.

The AFFF sensor unit is also equipped with an event recorder. The event recorder has a circular paper chart that makes one rotation every 31 days. The pen on the event recorder is activated when the AFFF sensor detects foam (i.e., while the output relay is closed). The pen is de-energized when the output relay is opened. The event recorder produces a permanent record of when a "foam event" occurred and how long the event lasted.

Photos of the exterior and interior of the AFFF sensor unit are presented in Figures 13,14,15, and 16. Figure 13 shows the unit in its enclosure. Figure 14 shows the details of the front panel of the unit. Figures 15 and 16 show the backside of the front panel and the subpanel respectively.

The control logic is presented in ladder logic form in Appendix A and a wiring diagram of the programmable logic controller is presented in Appendix B.

The AFFF sensor installed at Naval Station Mayport contains an additional feature not found in the laboratory prototypes. The sensor system contains an additional solenoid valve (and controller modifications) to permit a sample of the waste water to be collected each time the sensor is activated (i.e., the output relay is latched). When the high set point is reached and the latching relay is closed, the solenoid valve is opened for a few seconds to divert about 500 cu cm of the waste water into a sample collection vessel. The samples can subsequently be tested using chemical analysis methods to estimate the amount of AFFF in the sample. The Mayport installation is shown in Figure 17.

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Float Rise Time (Vented)

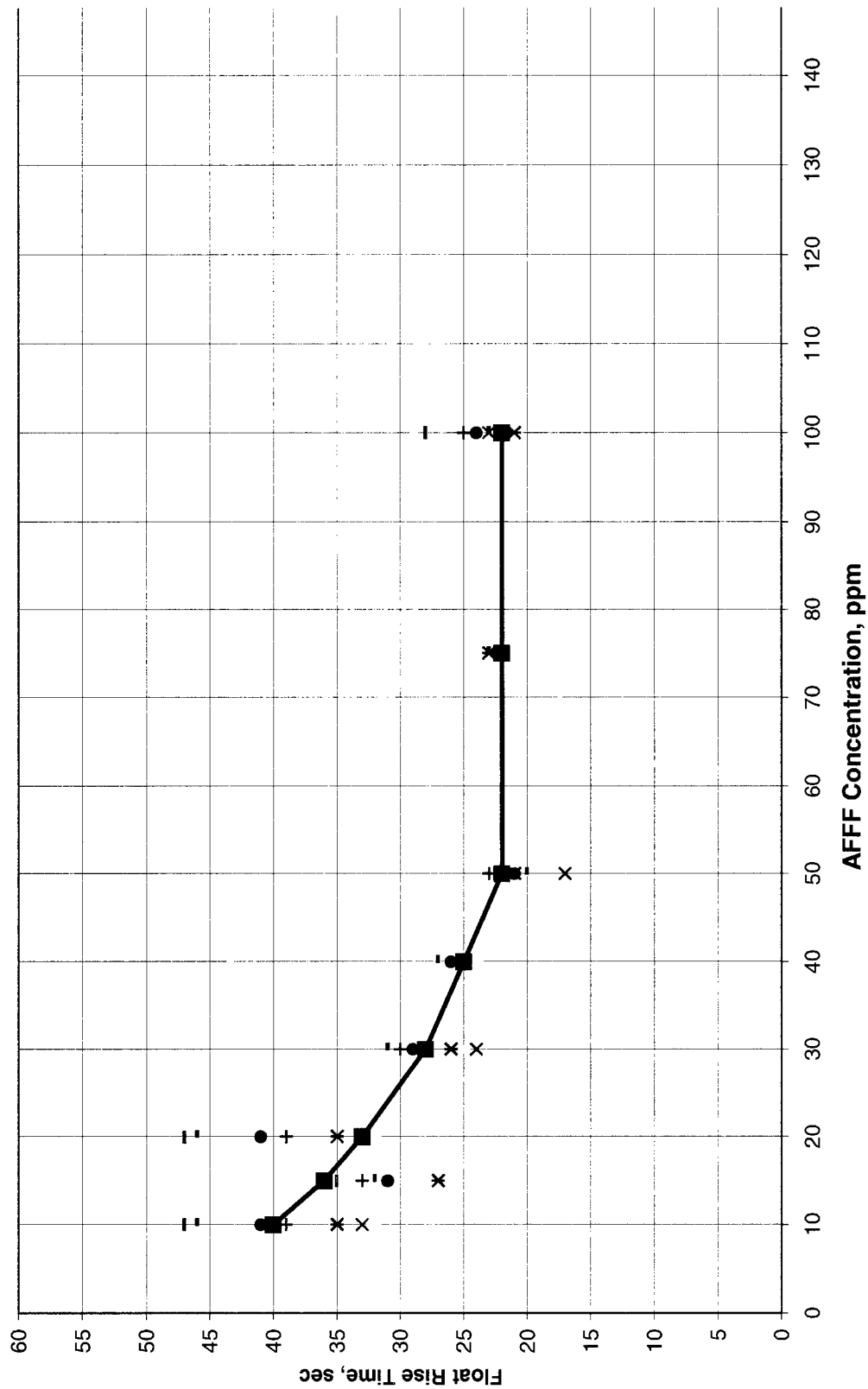


Figure 12. Sensor calibration curve.

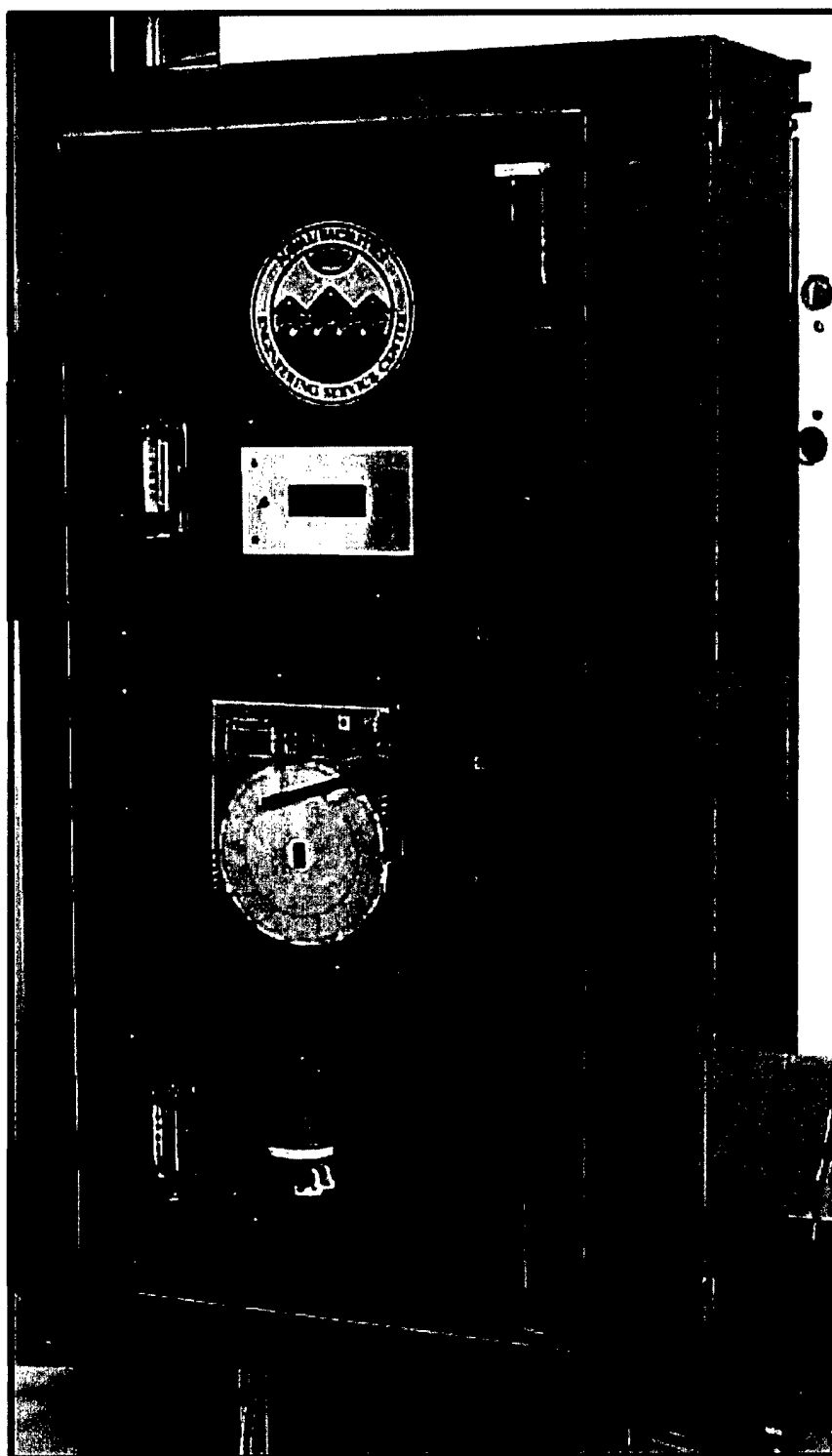


Figure 13. AFFF sensor in enclosure.

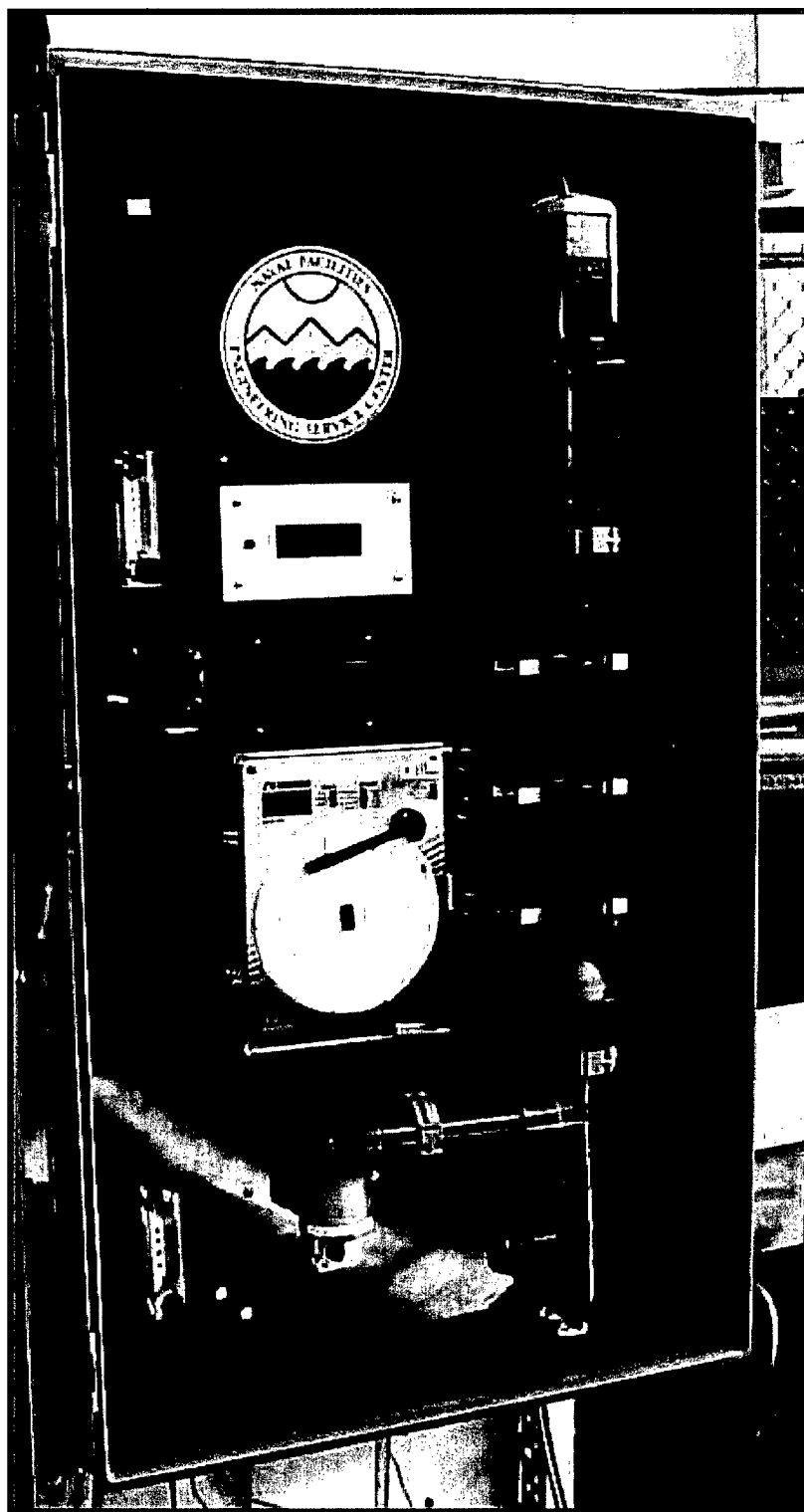


Figure 14. Detail of front panel of AFFF sensor.



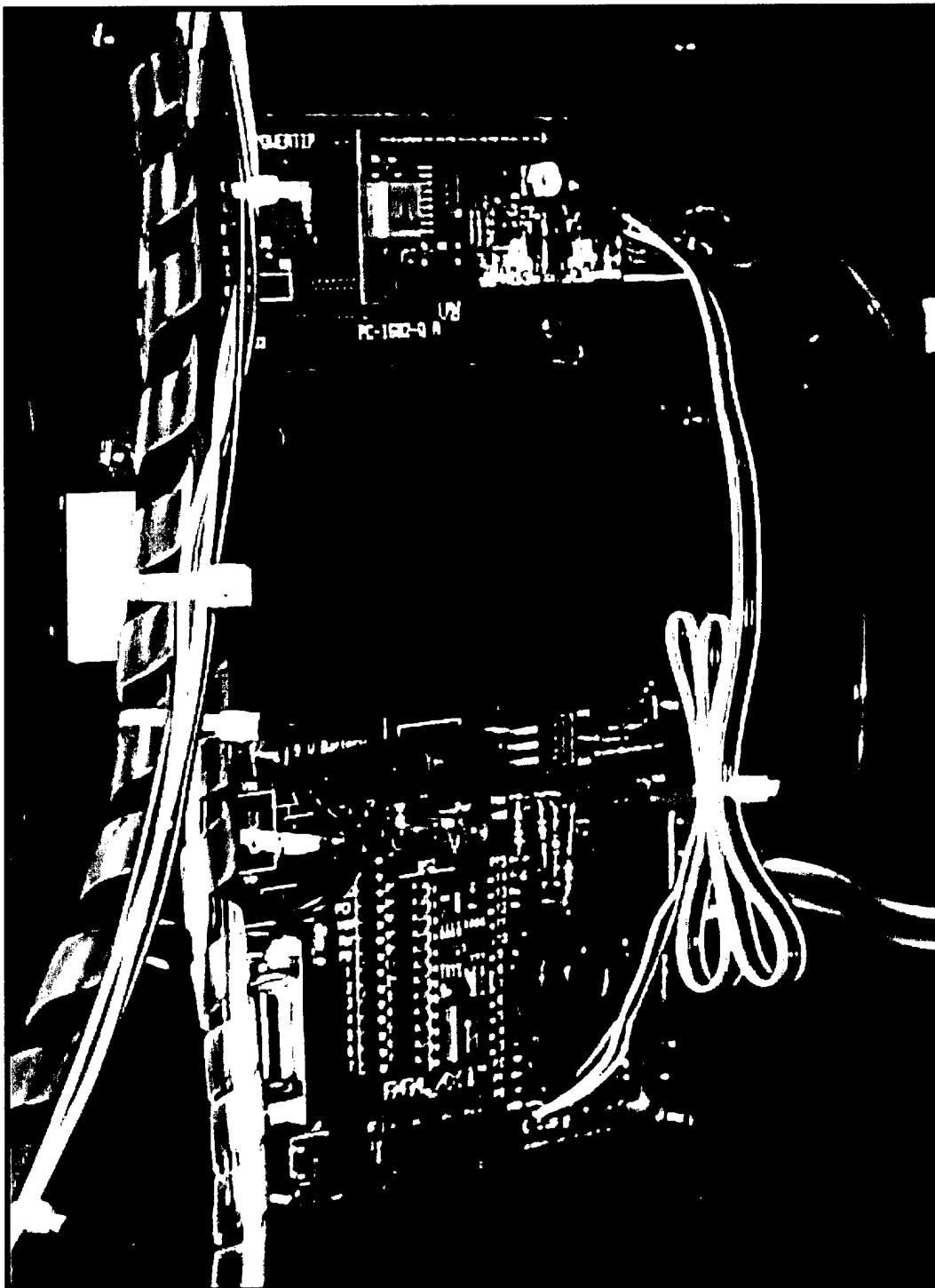


Figure 15. Back of front panel of AFFF sensor.

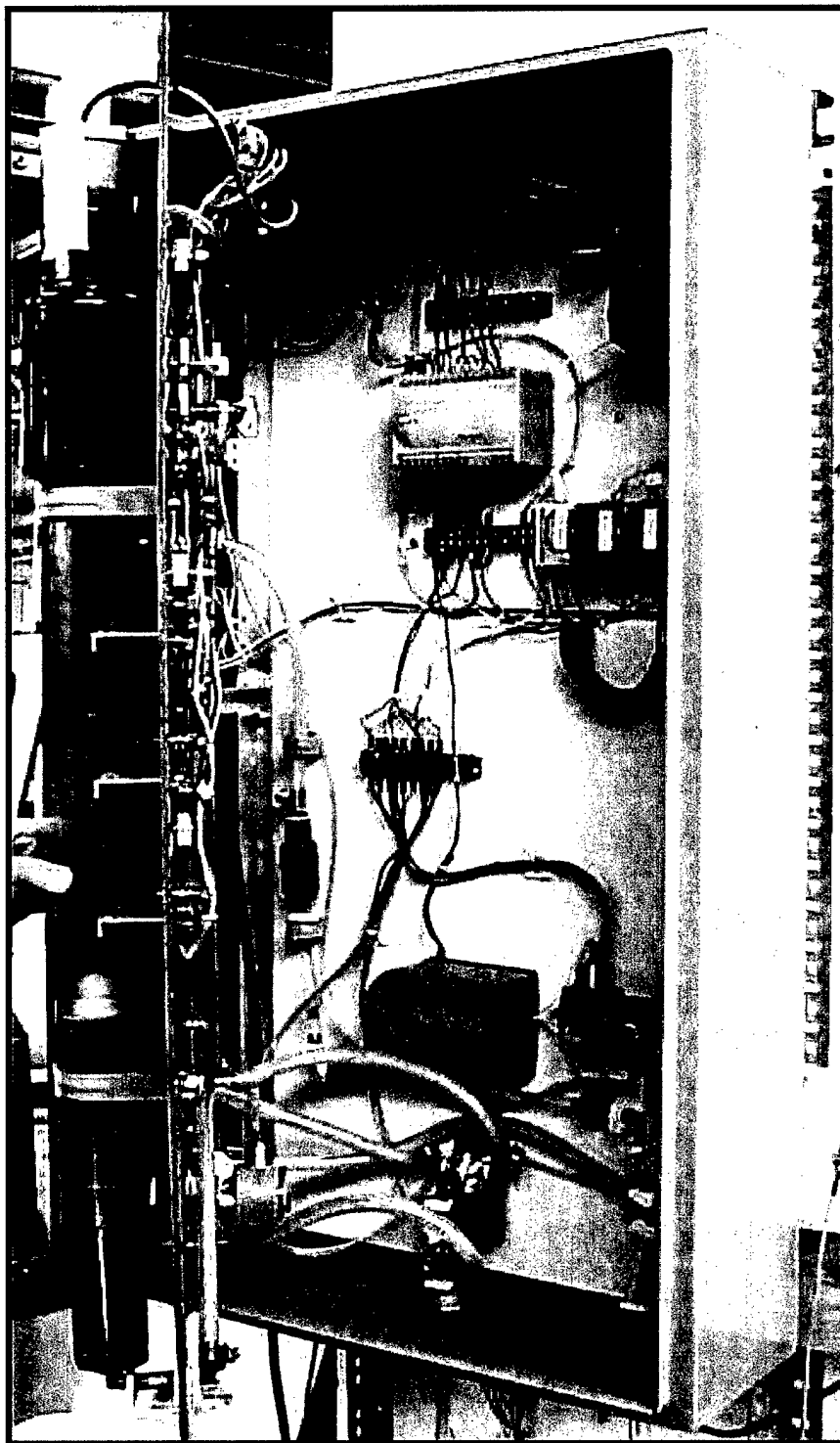


Figure 16. Detail of sub-panel of AFFF sensor.

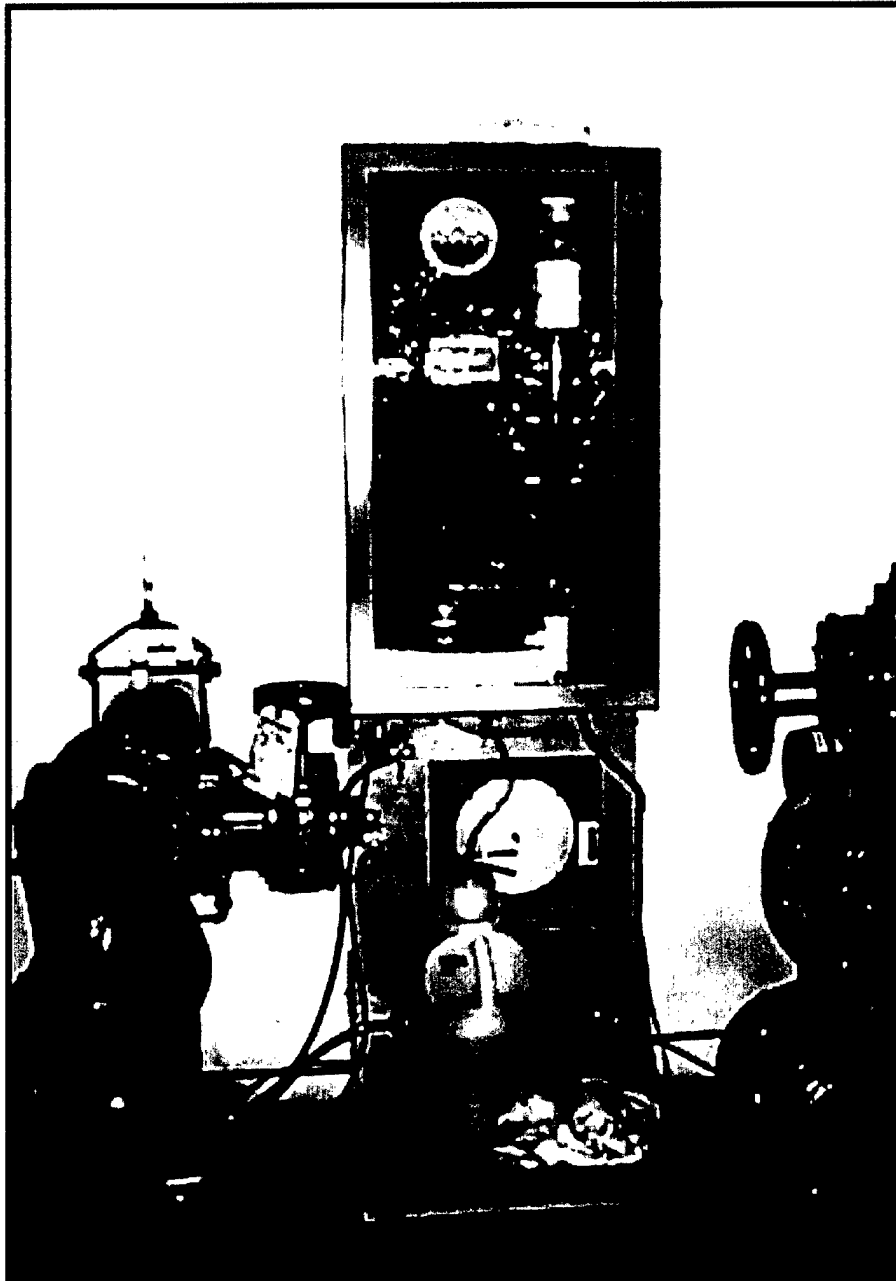
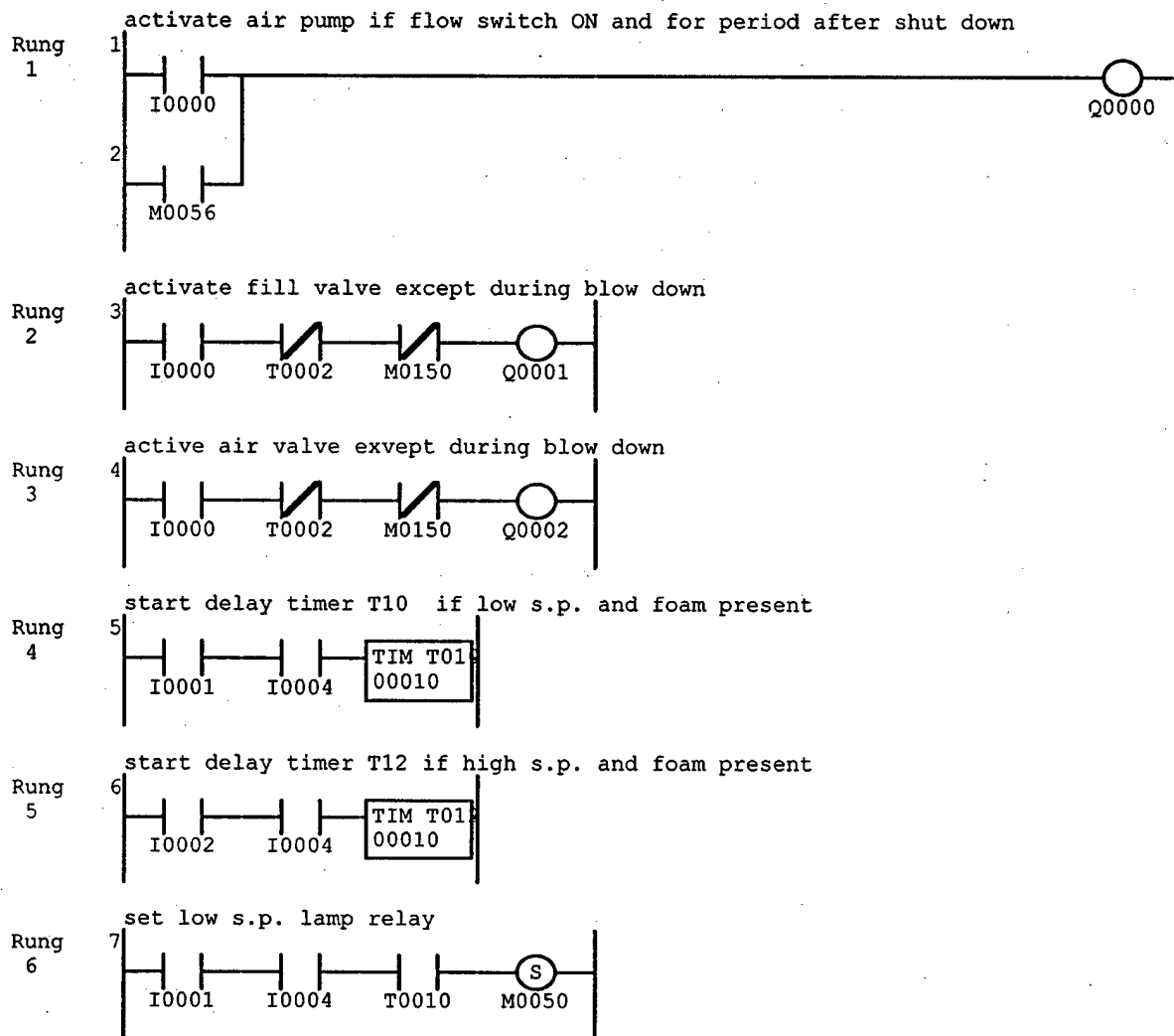


Figure 17. NS Mayport AFFF sensor installation.

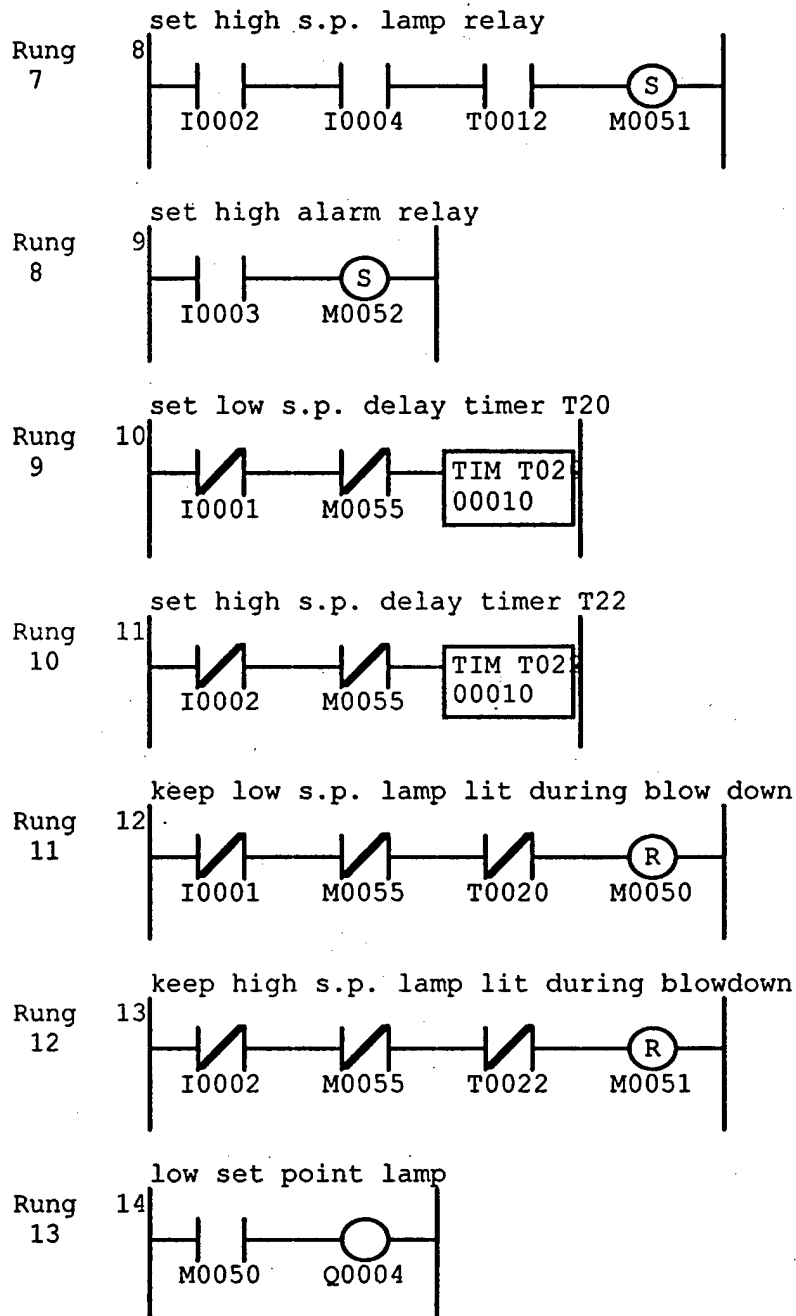
APPENDIX A

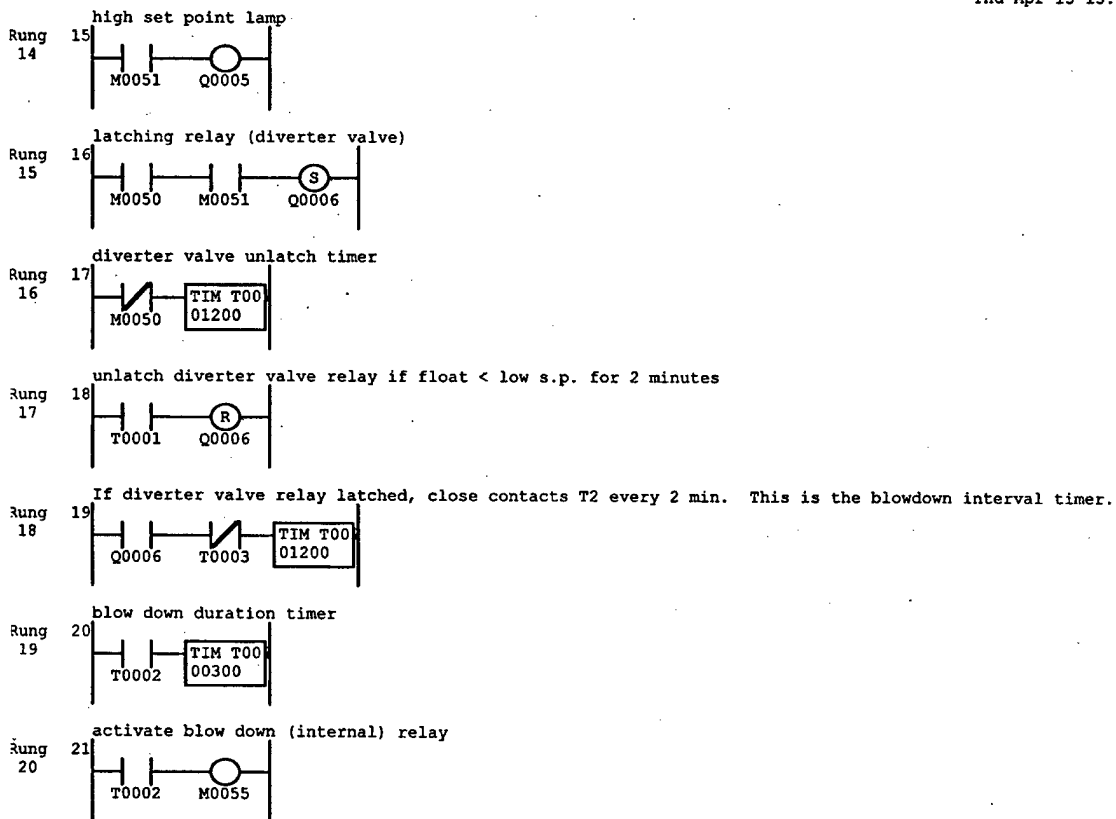
Control Logic Presented in Ladder Logic Form

A:\MAYPORT2.LDR



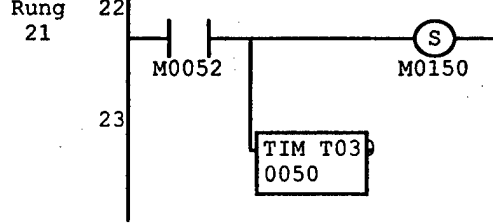
A:\MAYPORT2.LDR



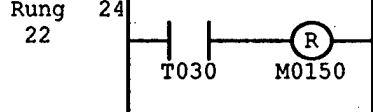


A:\MAYPORT2.LDR

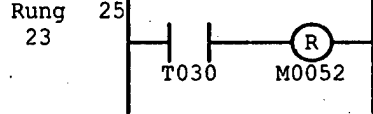
set internal relay M150 when high alarm s.p. is reached. Start timer T30



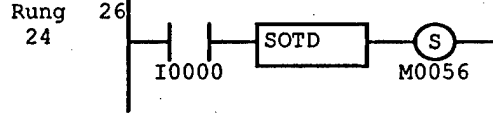
reset internal relay M150 when timer T30 contacts close



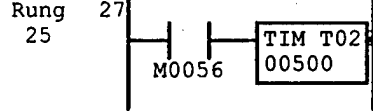
reset internal relay M52 when timer T30 contacts close



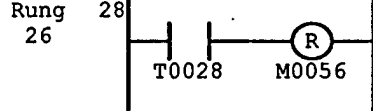
set internal relay M56 on down transition of flow switch.



start timer T28. Keeps air pump operating for brief period after flow stops

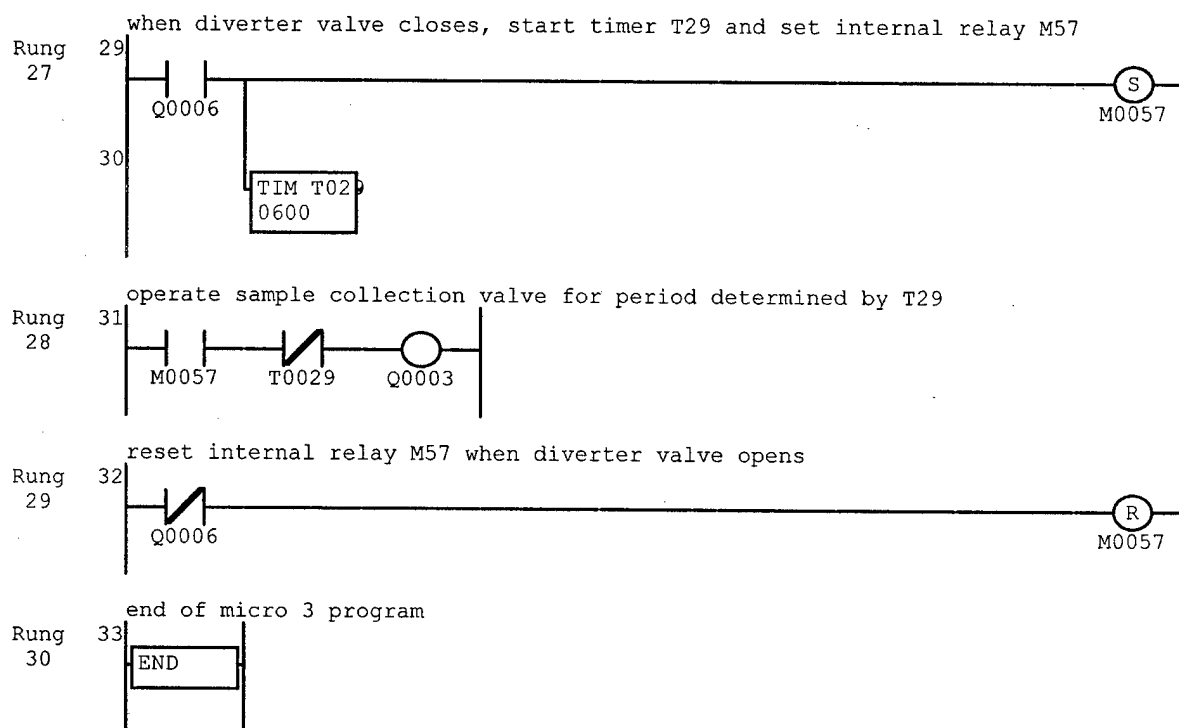


reset internal relay M56 and stop air pump





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## APPENDIX B

### Wiring Diagram of Programmable Logic Controller

